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Evaluation of the carbon adsorption method with parallel solvent extraction studies

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Department:

EVALUATION OF THE CARBON ADSORPTION METHOD WITH PARALLEL SOLVENT EXTRACTION STUDIES

BY

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ABSTRACT

In spite of the importance of the carbon adsorption method (CAM) in determining drinking water quality and its wide use in research and plant control studies, little work has been undertaken to quantitatively and qualitatively evaluate the method, especially under field conditions. This investigation was, therefore, undertaken in order to develop a test system consisting of equipment and procedures which would make possible the field evaluation of the carbon adsorption method by parallel solvent extraction studies, and to employ this system in preliminary field investigations to establish guidelines for the experimental conditions required for its effective application.

The test system developed in this study consisted of a sand filter and four carbon filters connected in series; a raw water pump; an acid storage tank and acid pump; sample outlets and storage reservoirs located before and after each filter unit; and associated flow meter, pressure gage, valves and piping. Organic micropollutants were recovered from a subsurface water source (Meramec Spring) by carbon adsorption at the natural (7.1) and an adjusted pH (2.5) and were eluted from the carbon with chloroform and benzene. Raw water and filter effluent samples, composited over appropriate periods, were solvent extracted with chloroform and benzene at appropriate pH levels (7.1, 2.5, and 10.0).

The test system proved to be satisfactory for the field evaluation of the CAM and enabled the monitoring of the trace organics in the influent to and effluent from the carbon filters. Preliminary evaluation studies indicated that the CAM had a low total efficiency for recovering trace organics, however, further research is needed in order to fully evaluate the method and establish its limitations.

ACKNOWLEDGEMENT

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I. INTRODUCTION

The presence of organic micropollutants, including pesticides, in surface and subsurface water is creating considerable concern. These organic materials are contributed from several sources, such as domestic and industrial wastes, agricultural runoff, accidental spillage, and the decomposition of natural products (1,2). Although present in water at minute concentrations, trace organics are often responsible for taste and odor, color, and toxicity.

The possibility that trace organics may deteriorate the aesthetic quality of the water, their resistance to biodegradation and conventional water treatment which enables them to concentrate during the recycling needed to meet increased water demands, and our inability to fully define the chemical and toxicological nature of these materials have necessitated the establishment of limiting concentrations for organic pollutants in drinking water supplies. These limits include a maximum permissible concentration of 200 μg/l for carbon chloroform extract set by the Public Health Service (PHS) Drinking Water Standards (3), and goals of 40 and 100 μg/l for carbon chloroform extract (CCE) and carbon alcohol extract (CAE), respectively, adopted by the American Water Works Association (AWWA) (4).

Both the PHS standard and the AWWA goals depend upon the carbon adsorption method (CAM) for recovering the trace organic pollutants from the water. This method was developed by the Public Health Service in the early 1950's (5) and has been included as a tentative method in Standard Methods (6, p.215). It consists of passing a known volume of water (usually 5,000 gallons) through an 18 inch by 3 inch diameter cylinder filled with activated carbon at a flow

rate of 0.5 gpm and eluting the organics from the carbon by serial extraction with chloroform. Chloroform was chosen as the solvent because it had been shown (5) that the chloroform-soluble materials contained the most odorous taste organics.

Several modifications have been applied to the CAM in an effort to increase the recovery of trace organics. These modifications have included sequential extraction with other solvents to enable the recovery of organic materials not eluted with chloroform, larger size carbon filters to allow the sampling of greater volumes of water in a shorter period of time, and pH adjustment of the water prior to filtration to aid the adsorption process. In addition, two or more carbon filters have been employed in series in order to facilitate the recovery of organics not adsorbed on the first filter, or provide for further adsorption following pH adjustment.

In spite of the importance of the CAM in determining drinking water quality and its wide use in research and plant control studies, little work has been undertaken to quantitatively and qualitatively evaluate the method, especially under field conditions. However, concern has been expressed in the literature over the ability of the carbon to adsorb all of the organics present in the water being sampled or the ability of the solvent to elute all the adsorbed organics, as well as the possibility of alteration of the organic materials while on the carbon. According to Hoak (7), Middleton and associates have studied the recovery of phenol under laboratory conditions and found that the adsorption efficiency ranged from 30 to 99 percent and the recovery efficiency from 61 to 77 percent, giving an overall recovery in the range of 19 to 77 percent. Hoak (7) has

also found that phenol adsorption on activated carbon was at least 98 percent with desorption as low as 47 percent.

Although the studies utilizing phenol have provided a partial insight into the efficiency of the CAM, it must be recognized that the organic pollutants which are present in natural waters are very complex materials and would not necessarily behave similarly to phenol. Consequently, there is a need to evaluate the CAM under actual field conditions. The basic difficulty encountered with such studies is the lack of instrumentation capable of directly measuring the total trace organics at the levels that are usually found in water without requiring prior concentration. However, another approach might be possible using a recovery method, such as solvent extraction, which does not depend on carbon adsorption to monitor the concentration of trace organics in the influent to and the effluent from the carbon filters.

Solvent extraction is receiving increased attention as a means of recovering trace organics, and has been adopted by the American Society for Testing and Materials (ASTM) as a tentative method (8). It consists of stirring the water with a solvent to transfer the organic materials from the water to the solvent phase, separating the solvent phase, and evaporating off the solvent to obtain the organic extract.

The purpose of this investigation was to develop a test system consisting of equipment and procedures which would make possible the field evaluation of the carbon adsorption method by parallel solvent extraction studies, and to employ this system in preliminary field investigations to establish guidelines for the experimental conditions required for its effective application.

The test equipment developed in this study consisted of five filter units (each containing 0.196 cubic feet of filter media) connected in series; one of these units was to be used as a sand filter when the water was turbid and required pretreatment, or as a stand-by carbon filter when a different pretreatment method was used or pretreatment was not necessary. Provisions were made for the continuous acidification of the water and the collection of samples for solvent extraction studies. Field investigations were conducted at Meramec Spring, Missouri. Carbon adsorption studies were made at the natural pH of the water and at a pH value of 2.5, and solvent extraction studies were performed at the natural pH as well as pH values of 2.5 and 10.0. Chloroform and benzene were the solvents employed to elute the concentrated organics from the carbon and to extract the trace organics directly from the water.

II. REVIEW OF LITERATURE

The purpose of this literature review is to present information pertinent to the evaluation of the carbon adsorption method for recovering and concentrating organic micropollutants in water. The review also contains information concerning both the standard carbon adsorption method (CAM) and its modifications and the batch-type solvent extraction method (SEM) which served as a basis for the development of the test equipment and procedures incorporated in this study.

A. CARBON ADSORPTION METHOD

This method, which is widely used in the United States, was developed at the Robert A. Taft Sanitary Engineering Center (5,9) and has been adopted as a standard method for the recovery of organic contaminants in water (6, p.214). It consists of passing 3,000 to 5,000 gallons of water upward through a vertically oriented filter, 18 inches high and 3 inches in diameter, containing 9 inches of fine (+30 mesh) activated carbon between two layers of coarse (4 x 10 mesh) activated carbon each 4.5 inches in thickness. The flow rate through the filter is from 0.25 to 0.5 gpm providing a contact time of 4.4 to 2.2 minutes, respectively. After the desired volume of water has been filtered, the carbon is removed, dried, and then serially eluted with chloroform to desorb the organic materials.

Several modifications of the standard CAM have been used by various investigators primarily to enable greater recoveries of a wider spectrum of organic substances in water in a shorter period of time. These modifications have included sequential elution of

the carbon with additional solvents to recover organics other than chloroform-soluble materials, two or more filters in series to extract organics not recovered on the first filter and allow for pH adjustment of the water, larger size filters to permit the sampling of greater volumes of water at higher filtration rates, and acidification of the water to enhance the adsorptive ability of the carbon. In addition, several pretreatment methods have been used with turbid waters to prevent clogging of the carbon filters.

A number of studies which have employed a modified CAM are summarized in Tables I and II. Table I presents information on the extraction system used as well as the source and volume of the water sampled, and Table II gives the quantity of organics recovered from each filter by sequentially eluting the carbon with different solvents. Increased amounts of organic contaminants were recovered under the conditions described; however, the data obtained in these investigations cannot be used to directly evaluate the CAM because the quantity and character of the organic materials in the influent to and the effluent from the filters were not determined.

B. EVALUATION OF THE CARBON ADSORPTION METHOD

Hoak (7) has summarized studies undertaken to evaluate the CAM using simple phenolic materials over a wide range of concentrations. He reported that Middleton and associates at the Robert A. Taft Sanitary Engineering Center used a procedure consisting of mixing 3.0 grams of Nuchar C-190 with a series of 200 ml solutions containing from 0.1 to 3.0 grams of phenol; after 30 minutes of stirring the mixtures were allowed to stand overnight; the carbon was then filtered off, air dried, and extracted with chloroform. They found

Table I

Modifications of the Carbon Adsorption Method
Summary of Sampling Data

Investigators	Source of Water Sampled	Sampling System		Activated Carbon*			Sampling Data			Ref.
		Pretreatment	No. of Filters	Volume cu. ft.	% Fine	% Coarse	Flow gpm	Detention Time** min.	Volume of Water gal.	
Middleton, et al.	Cincinnati Tap Water	None	2***	0.073		100	0.25	3.5	7,300#	10
Middleton, et al.	Ohio River	Sand Filter	2	1.24	50	50	7.0	1.3	121,900	11
Dornbush & Ryckman	Missouri River	Sedimentation and Diatomite Filtration	2***	1.30	60	40	5.0 to 7.5	1.3 to 2.0	96,400	12
Myrick & Ryckman									91,300	13
Spicher & Skrinde									103,000	14
Grigoropoulos & Smith	Meramec Spring	None	3	1.5	50	50	5.2	2.2	## 131,000	1, 15

*Each filter; Fine: +30 mesh Nuchar C-190, Coarse: 4 x 10 mesh Cliffchar; two equal layers of coarse carbon, one on the top and one on the bottom of the fine carbon layer.
**Computed for each filter unit.
***Water was acidified before entering the second filter.
#Average of four runs ranging from 5,160 to 11,640 gal.
##Average of two runs of 129,000 and 133,000 gal.

Table II

Modifications of the Carbon Adsorption Method
Summary of Recovery Data

Investigators	Filter No. 1					Filter No. 2					Filter No. 3					Ref.
	pH	CCE	CAE	CAcE CBE#	CBE CAcE*	pH	CCE	CAE	CAcE CBE	CBE CAcE	pH	CCE	CAE	CAcE CBE	CBE CAcE	
	Trace Organics Recovered, grams															
Middleton, et al.	8.5	2.7	---	---	---	3.4	4.2	---	---	---	---	---	---	---	---	10
Middleton, et al.	**	41.0+	100.0+	---	---	**	41.0+	100.0+	---	---	---	---	---	---	---	11
Dornbush & Ryckman	8.1	27.7	85.6	---	---	2.9	28.4	115.5	---	---	---	---	---	---	---	12
Myrick & Ryckman	8.1	28.8	112.5	---	---	3.5	23.9	195.8	---	---	---	---	---	---	---	13
Spicher & Skrinde	7.7	27.9	65.1	---	---	3.2	23.0	151.0	---	---	---	---	---	---	---	14
Grigoropoulos & Smith	**	20.4	30.8	7.0 0.2	2.9 3.1	**	8.1	28.0	9.1 0.3	4.8 6.8	**	5.3	16.7	8.6 1.4	2.8 5.0	1, 15

#Extraction sequence: Chloroform, ethanol, acetone, benzene.
*Extraction sequence: Chloroform, ethanol, benzene, acetone.
**At natural pH.
+Total recovery by the two filters which were eluted simultaneously.

that adsorption ranged from 99 to 30 percent and decreased as the phenol concentration increased, and that desorption ranged from 77 to 61 percent; and reported that phenol did not seem to change while adsorbed on the carbon. Golding and associates, also at the Taft Center, reported adsorption of 1.0 gram of phenol on 15 grams of activated carbon and 72.7 percent recovery of the phenol by elution with chloroform. Hoak (7) repeated the experiments of Middleton and associates using 0.5 grams of phenol and 3.0 grams of carbon and found that the adsorption efficiency ranged from 98.0 to 99.6 percent, while the desorption efficiency varied from 72.8 to 76.2 percent. However, when the carbon suspension was allowed to stand for a longer period of time (28 days rather than overnight) the desorption efficiency was decreased to 47.0 percent. This indicated that recovery decreased with time of contact of the phenol and carbon and was attributed by Hoak to possible phenol oxidation on the active carbon surface and bacterial degradation.

Several serial extractions are required to elute a significant percentage of the adsorbed materials. Studies conducted by Middleton, et al. (10) have shown that the rate of recovery of the organics from the carbon depended primarily on the type of the adsorbed materials and the extent of saturation of the carbon. When activated carbon which had been used to recover organic materials from a raw water was extracted with chloroform, the following results were obtained.

Period of Extraction hours	Extract Recovered grams	%
8	15.546	91
24	1.065	6
46	0.519	3

As can be seen from these data, 97 percent of all the material eluted in 46 hours was recovered in 24 hours.

Several investigators have commented on the efficiency of the CAM on the basis of their evaluation of CAM data. Hoadley (16), after reviewing data from the FWQA (formerly PHS) Water Pollution Surveillance System, concluded that the adsorptive capacity of the carbon may have been exhausted and recommended that the amount of carbon be increased or the flow rate decreased. The Water Pollution Surveillance System (17) was established in 1957 to collect and disseminate basic data on chemical, physical, and biological water quality, and by 1966 had expanded to 131 sampling stations throughout the United States. As part of this system, trace organic pollutants are recovered at these stations by means of a standard (0.073 cubic foot) activated carbon filter and elution with chloroform and ethanol.

Atkins and Tomlinson (18) conducted studies to measure the variation of the concentration of organic pollutants in the Missouri River using a modified and a standard carbon filter. The operational data were as follows:

Filter	Carbon Volume cu. ft.	Pretreatment	Length of Filter Run days	Flow Rate gpm	Volume of Water gal.
Modified	~1.3	Sedimentation	0.5	<7	2,800-5,000
Standard	0.073	Sand Filtration	14	0.25	5,000

The carbon was sequentially eluted with chloroform and ethanol. Sixteen one-day sampling runs were made using the modified filter and two runs were made using the standard filter during a period of approximately one month. It was found that the average values of

the daily CCE and CAE were two and three times as high as the CCE and CAE obtained from the standard filter over a period of 14 days. This variation was attributed to the large carbon volume used in the modified filter, which was 20 times as large as the standard filter, and the fact that the modified filter was recharged daily, thereby lessening the possibility of exhausting the adsorptive capacity of the carbon.

Greenburg, et al. (19) performed studies to evaluate the CAM and determine its reproducibility and efficiency. Five standard carbon filters containing 100 percent fine (+30 mesh) carbon were operated in series or in parallel. Water from a 900 million gallon reservoir filled with Sacramento River water was passed through the filters at a rate of 0.5 gpm. Volumes of 1,500, 3,000, and 6,900 gallons were passed through the five filters in series during three separate runs, and volumes ranging from 450 to 6,600 gallons were passed through the filters in parallel during another run. The carbon from the various units was sequentially eluted with chloroform and ethanol. Assuming that the total organic material obtained from the five filters in series represented 100 percent of the organics in the sample, these investigators estimated that the CCE and CAE recovery efficiencies of the first filter decreased from maximum values of 67 and 49 percent when 1,500 gallons were sampled to minimum values of 42 and 29 percent when 6,900 gallons were filtered. Three or four filters in series were required for 90 percent recovery. The quantities of CCE and CAE materials recovered from the filters which were operated in parallel differed by less than 5 percent, indicating that the CAM was a reliable sampling procedure. On the basis of their

findings, Greenburg, et al. (19) recommended that two standard CAM units be operated in series when flow rates of 0.25 to 0.5 gpm are used, and that the maximum sample volume be reduced to 2,500 gallons.

Grigoropoulos and Smith (1) in their studies of trace organics in Missouri waters employed three large carbon filters in series (see Table I, p.7) to sample a spring and two deep wells. They concluded that the number of filters required to effectively recover organics from water depended on the source of the water and the nature and concentration of the organics. One filter was found adequate for the well waters; however, considerable additional material was obtained with the second and third filter when the spring water was sampled. The concentrations of the CCE and CAE recovered with each filter in two runs at the spring were as follows:

	CCE & CAE Recovered, µg/l	
Filter No.	Run No. 1	Run No. 2
1	78.0	128.1
2	50.4	95.1
3	24.3	64.4

These investigators noted that Filters No. 2 and 3 of Runs No. 1 and 2 recovered approximately 27 and 33 µg/l, respectively, less than their preceding unit, and estimated that while the three units effectively removed all the trace organics from the water in the first run, a significant quantity of materials was not recovered in the second run and a fourth unit would have been necessary for complete recovery.

These evaluations have been based upon the amount of materials obtained by a number of filter units in series and the assumption

that all the organics in the water sample had been recovered. However, without knowing the actual organic concentrations going into and leaving the filters, the efficiency of the CAM cannot be fully evaluated. It is necessary to use a procedure which can determine the concentration of the organic contaminants in the water before and after each filter. The solvent extraction method may serve such a function.

C. SOLVENT EXTRACTION METHOD

The batch-type solvent (liquid-liquid) extraction method (SEM) has been recently adopted as a tentative method by the American Society for Testing and Materials (8). This method consists of mixing the water for two minutes with an appropriate solvent to transfer the organic materials from the water to the solvent phase, separating the solvent phase, and evaporating off the solvent to obtain the organic extract. The type of solvent to be used is not specified other than it must be immiscible with water; however, a total solvent to sample ratio of 1 to 12, added in three equal increments, is specified. Extractions are sequentially performed at neutral, acid (pH 3), and alkaline (pH 11) conditions to enable a general classification of the organic constituents and a more complete separation of the total organic content of the water sample.

Skrinde and Tomlinson (20) have discussed the recovery of trace organics using the SEM. Benzene was used to extract samples of Missouri River water which were fortified with 0.4 mg/l of the pesticide lindane. Recoveries of 79 and 68 percent were obtained when benzene to water ratios of 1 to 10 and 1 to 20 were employed.

A total solvent to water ratio of 1 to 10 and three serial extractions were successfully employed in extracting trace organic materials from Missouri River water using chloroform, and the following recoveries were obtained at different pH levels.

Sample	Trace Organics Recovered, µg/l pH 2	pH 7	pH 11
1	900	570	420
2	900	770	450
3	850	570	600

They reported that the formation of an emulsion between the solvent and water phases was a major operational difficulty; this problem was intensified in the presence of turbidity in the water but was greatly reduced at the lower pH value.

In order to reduce the solubility of the organics in the water, Caruso, et al. (21) added sodium chloride to 6 liter water samples which were sequentially extracted with reagent grade ethyl ether after pH adjustment to 4 and 10. A solvent to water ratio of 1 to 3 was used. Following extraction, the volume of the sample was reduced and the extracts were subjected to gas chromatographic analysis to provide a "fingerprint" of the organic compounds in the water. Baker and Malo (22) also employed the SEM to concentrate trace organics in water prior to gas chromatographic analysis. The samples were sequentially extracted with ethyl ether (ratio of 1 to 3) at pH values of 3, 7, and 10 in order to make possible the separation of the acid, neutral, and basic compounds.

Hoak (7) used the solvent extraction method with a variety of solvents, including chloroform, methyl isobutyl ketone, carbon tetrachloride, benzene, petroleum ether, pentane, isopropyl ether,

and heptane. Ten and 20 ml portions of the various solvents were mixed with a 500 ml solution of 100 µg/l phenol in distilled water and shaken for 1 and 5 minute periods in a separatory funnel. The methyl isobutyl ketone proved to be the best, however, it was difficult to separate from the organics.

Ryckman, et al. (23) in their review of new techniques for the evaluation of organic micropollutants have pointed out that the SEM gives greater organic yields than the standard CAM. The SEM can be completed in 2 to 4 hours, whereas the standard CAM requires 3 weeks. They also reported certain drawbacks to the method, including the difficulty with sample turbidity which causes emulsions, the need for a solvent that is immiscible in water, and the limited volume of water which can be sampled.

III. FIELD TEST SYSTEM

A primary objective of this investigation was the development of a test system which would make possible the field evaluation of the carbon adsorption method (CAM). The solvent extraction method (SEM) was selected as the means for monitoring the influent and effluent concentration of trace organics to and from the carbon filters, thereby enabling the direct evaluation of the efficiency of the CAM. To accomplish this objective a field test system which allowed parallel, concurrent carbon adsorption and solvent extraction studies was designed and constructed.

A. DESIGN FEATURES

After reviewing the literature available in this area of study and considering the overall objective of this investigation, the desirable design features of the test system were established. The standard CAM employs small filters (0.073 cubic foot) requiring a long sampling period (14 days for a 5,000 gallon sample) at a 0.25 gpm flow rate (4.4 minute contact time); several investigators have used large filters (1.2 to 1.5 cubic foot) that were difficult to handle, but gave large organic samples in a shorter period of time. These large filters can sample the same volume of water as the standard filter in less than one day using flow rates of 5.0 to 7.5 gpm (1.3 to 2.2 minute contact time). It was decided that the filters used in this study should incorporate the basic concepts of both the large and small filters, and yet be inexpensive, mobil, versatile, and adaptable to the many different water supplies that would be sampled when evaluating the method. Sampling conditions may require that the filters be subjected to the high pressures

encountered at water supply pumping stations, as well as to transportation in trailers or other such vehicles. For this reason, the units should be ruggedly constructed and durable. Location of the test equipment at bridge sites, which offer accessibility and protection, may necessitate suspending the equipment under the bridge and, therefore, require that it forms an integral and compact structure.

The number of filters in series is another important consideration. There is ample evidence in the literature that more than one filter in series are often needed in order to recover a major portion of the organic materials in the water. A number of filters in series also offers the opportunity for reducing the pH of the water filtered through some of the units, thus gaining additional recoveries not possible at natural pH levels. Acidification of the water involves special precautions for storing and injecting the acid solution and for protecting the equipment from corrosion.

The sample turbidity will vary with each sampling location, and pretreatment must be incorporated to insure continuous operation. The pretreatment facility must comply with the overall compactness, flexibility, ease of assembly, and durability required of the other test units.

The system should be equipped with a pump which has a range of pressures sufficient to meet the friction losses and elevation requirements dictated by the topography of the sampling location. This pump should also be capable of providing the flow rates dictated by the desirable sample volume and available sampling time.

Sampling outlets must be provided at key points within the system for the collection of samples to be used in the monitoring studies by the SEM. Storage reservoirs should be provided for each of these outlets to facilitate the collection of a composite sample over an appropriate period of time. These reservoirs should be large enough to collect a sufficient size sample for the solvent extraction studies. The following guidelines for sample size selection have been presented by ASTM (8).

Sample Size, liters	Organic Matter in Sample, mg/l
25	0.1
5	0.1 to 0.5
2	0.5 to 5.0
1	5.0 to 50

B. FIELD TEST SYSTEM

The test equipment developed in this study is shown in Figure 1. It consisted of a sand filter (not shown) and four carbon filters connected in series; a raw water pump; an acid storage tank and acid pump; sampling outlets and storage reservoirs located before and after each filter unit; and associated flow meter, pressure gage, valves, and piping.

The sand and carbon filter units were constructed from salvaged steel fire extinguisher bottles which were altered to give the desired arrangement. The dimensions and construction details of each unit are shown in Figure 2. These bottles were selected because of the pressures they could withstand, while being of a convenient size and weight for portability in field studies. The interior of the bottles was sand blasted in order to clean the metal, and then coated with two coats of epoxy primer (Phelan

a. Test Equipment Arrangement

b. Test Equipment on Location at Meramec Spring

Figure 1

Field Test System

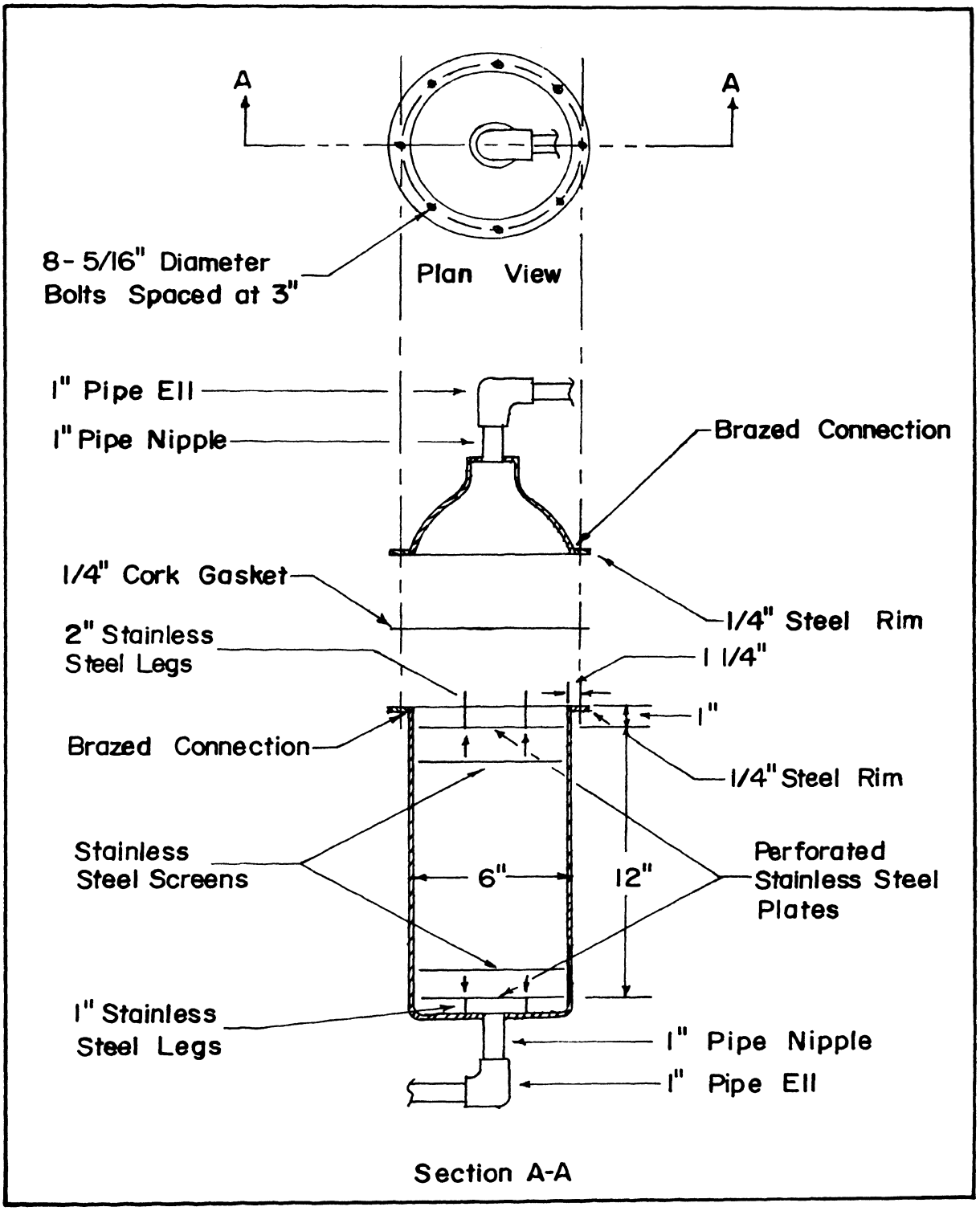

Figure 2

Sand or Activated Carbon Filter Unit

Faust No. 4051*) followed after 24 hours of drying by three coats of white epoxy enamel (Phelan Faust No. 3850*). This epoxy finish was selected as a coating because it was thought to provide an inert surface which would be resistant to corrosion due to the wet carbon and acidic conditions. Later on in the study, however, it was found that this finish was affected by the acid solution and maintained, even after prolonged periods, the characteristic odor of the solvent phase, indicating that the curing process might not have been completed. At the suggestion of a Phelan Faust representative (24) the units were placed in a drying oven at 210°F for 12 hours in an attempt to speed up the curing process; this treatment was not successful and another epoxy finish was sought. At the recommendation of the Phelan Faust representative, the Carboline Company was contacted and their representative (25) recommended and provided materials for a new finish which, in addition to being inert, did not contain high boiling point solvents not readily removed. The previous finish was removed by sand blasting and a new finish was applied. This finish consisted of a one coat application of epoxy primer (Phenoline No. 368**) followed after 24 hours of drying by a two coat application of epoxy finish (Phenoline X2301-114**). The units were then heat cured at 210°F for 24 hours. Two 40 x 40 mesh stainless steel screens supported by perforated plates were placed on the top and bottom of the carbon column to keep it in a packed state. Magnesium plates coated with the Phelan Faust epoxy finish

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*A product of the Phelan Faust Paint Mfg. Co., St. Louis, Missouri.
**A product of the Carboline Company, St. Louis, Missouri.

were used initially, but were later replaced with stainless steel plates. The location of the screens and plates formed a 0.196 cubic foot carbon column which was 6 inches in diameter and 12 inches high.

The pump and filter arrangement is shown in Figures 3 and 4. The sand filter (shown in Figure 3) would only be necessary when a turbid water sample is to be filtered. This filter could be back-washed simply by opening and closing appropriate valves before and after it. Because the sand filter was identical in construction details to the carbon filters, it could also be employed as a fifth or a substitute carbon filter when pretreatment was not necessary or was accomplished by other means (such as coagulation-sedimentation or diatomite filtration). The connections between the various units were all interchangeable so that the acid solution used for pH adjustment could be administered between any two of the filters in the series. The flow rate and pressure in the system could be regulated with a series of valves.

The water was supplied to the filters by a 3/4 horsepower centrifugal pump (Sears model 390.208*) on a 220 volt hook-up. The pump capacity was greater than would normally be required and provisions were made for by-passing the excess flow. The inlet facility consisted of a one inch galvanized pipe equipped with a screened foot valve. A Trident Triseal meter (Neptune style No. 3, 5/8 connections**) was used to measure the total volume of water passed through the system, and was placed between the first and second filter in order to protect it from the turbidity in the

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*A product of Sears, Roebuck and Company, Kansas City, Missouri.
**Purchased from the Folla Municipal Utilities, Rolla, Missouri.

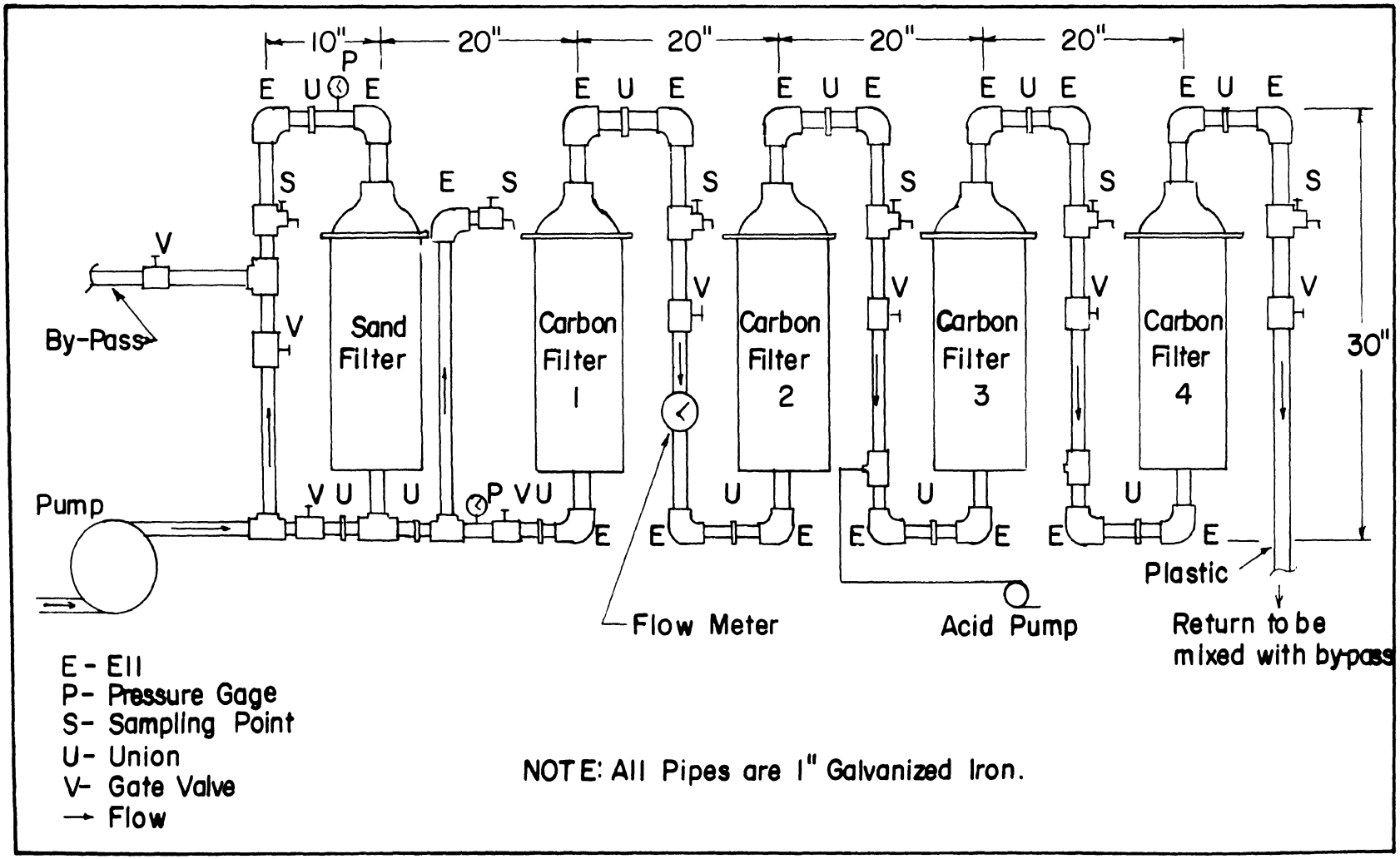

Figure 3

Pump and Filter Arrangement

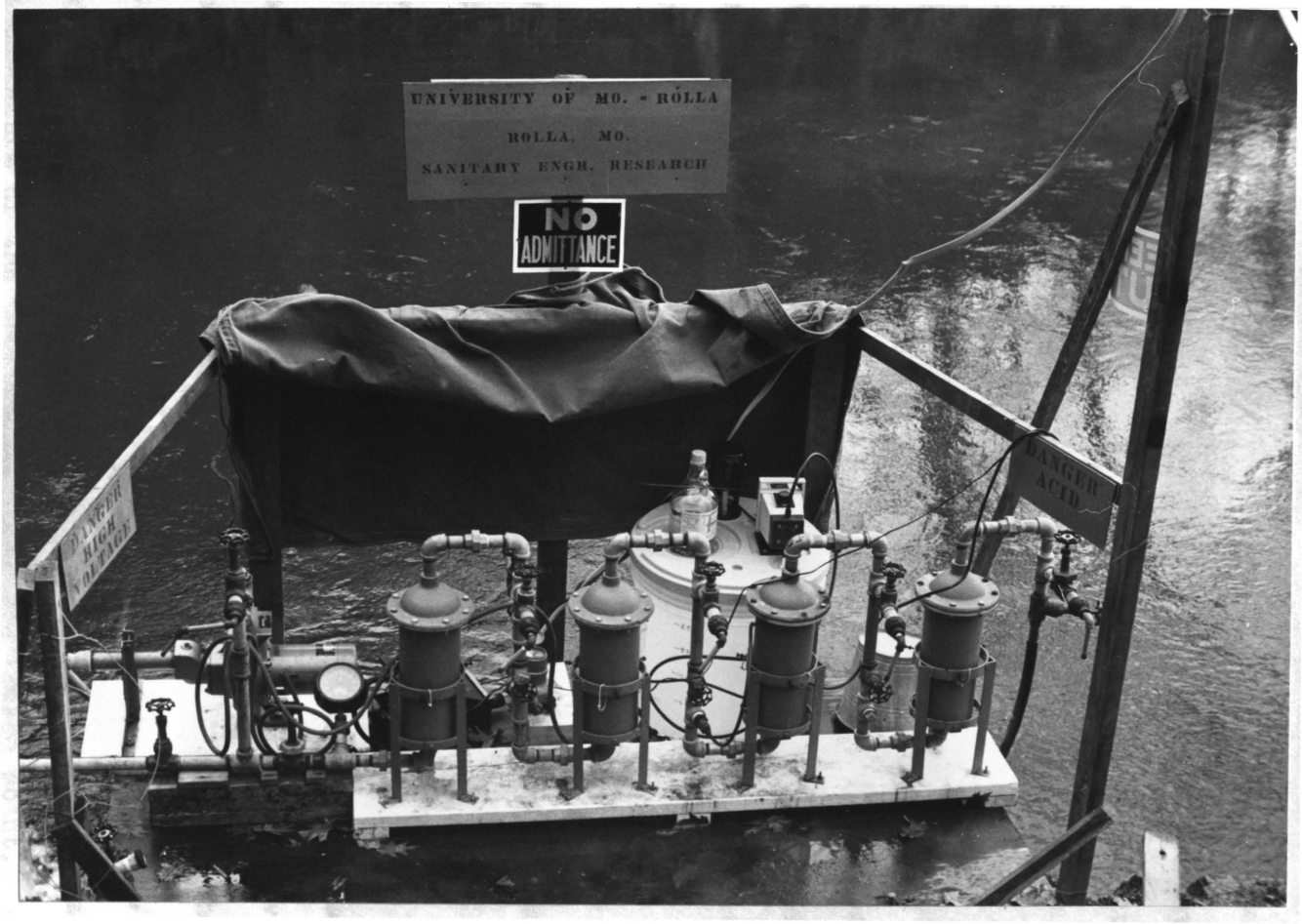

Figure 4

Pump and Filter Arrangement on Location at Meramec Spring

water or the low pH present after acidification. The meter could be closed off from the system by valving without affecting the flow through the system. This protected the meter from clogging by fine carbon while the filters were being flushed at the beginning of a run. A 16 foot section of one inch PVC pipe was provided to return the filter assembly effluent to the outlet of the by-pass pipe, and the combined effluent and by-pass flow were discharged downstream from the intake point.

A diaphragm pump (Wallace & Tiernan No. 94-110*) with a variable output was used to inject the acid solution into the system. It was used in conjunction with a Wallace & Tiernan 30 gallon polyethylene solution tank* with fiber glass cover and 1/20 horsepower solution stainless steel mixer.* The acidification assembly is shown in Figure 4.

Raw water and filter effluent samples were collected from appropriate sampling outlets and stored in 20 gallon reservoirs (galvanized garbage cans). Cans which received filter effluents after the water had been acidified were coated with the same epoxy finish used to coat the filter units in order to protect them from attack by the acid. The arrangement of the sampling outlets and reservoirs is shown in Figure 1a, p.19. In order to prevent freezing of the filter units, and especially of the sampling outlets and reservoirs, a small thermostatically controlled electric heater was employed to maintain the temperature of the test system above the freeze point.

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*Purchased from Lesco Division of Sidener Supply Co., Granite City, Illinois.

IV. EXPERIMENTAL STUDIES AND RESULTS

Organic micropollutants were concentrated and recovered from a subsurface water source (Meramec Spring) at the natural (7.1) and an adjusted pH (2.5) using the field test system previously described. Two sampling runs were made during this study; the first run was from July 10 to August 3, 1969, and the second run was from November 3 to November 29, 1969. Raw water and filter effluent samples composited over five day periods during the run were taken to the laboratory and solvent extracted sequentially with chloroform and benzene at appropriate pH levels (7.1, 2.5, and 10.0). At the end of a sampling run, the carbon was removed from the filters, dried, and sequentially eluted with chloroform and benzene. The solvents containing the concentrated organic materials were evaporated off and the extracts obtained.

A. LOCATION

Meramec Spring (Figure 1b, p.19) was chosen as the source of spring water to be sampled during this study. The spring is located 9 miles east of St. James, Missouri, on Route 8 and is reported to be the seventh largest spring in Missouri (26). The rock formation through which this spring flows is Van Buren Dolomite and there are many supply routes connected to surface feeders in the area south, west, and southwest of the spring. The average flow of the spring during the first run was 105 cfs, ranging from 100 to 110 cfs; during the second run the average flow was 81 cfs, ranging from 71 to 87 cfs (27).

Meramec Spring was selected as the sampling location because of its relatively close proximity to Rolla and the fact that it is

subject to surface contamination. In addition, trace organic pollutants have also been recovered from this spring by other investigators at the University of Missouri-Rolla (1,15,28) and their data were available for guidance in the development of this study and evaluation of its findings.

Locating the test equipment at Meramec Spring required some special preparations. A 4 foot wide and 8 foot long platform (Figure 1) was constructed of 5/8 inch exterior plywood reinforced with 2 x 4 members on the underside. It was supported over the water by two adjustable pipe jacks and was fastened to the shore with two steel stakes driven flush with the platform top. Wire twist braces were incorporated to stabilize and strengthen the platform. The field equipment was located on this platform and was covered by a canvas top; with this arrangement the equipment was protected from and did not interfere with the visitors to the spring. A temporary 220 and 110 volt hook-up was installed to provide the electricity needed for the operation of the pumps, mixer, and heater. A one inch galvanized pipe, which extended into the mouth of the spring and was equipped with a screened foot valve, served as the intake.

B. PROCEDURES

1. Field Sampling Procedures.

The carbon filters and all pipes, valves, and connections were cleaned with a mild Bon Ami solution and rinsed thoroughly with tap water. The filters were packed with 575 grams coarse* and 360 grams

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*4 x 10 mesh Cliffchar, a product of Cliffs Dow Chemical Co., Marquette, Michigan.

fine* activated carbon (50 percent each by volume) at the Civil Engineering Building, assembled into a series compound, and then transported as a unit to the sampling location. The total volume of carbon in each filter was 0.196 cubic feet and consisted of two layers of coarse carbon (3 inches each), one layer on either side of a layer of fine carbon (6 inches); this gave a 12 inch column of carbon through which the sample had to pass. Teflon tape was used as a pipe thread sealant to provide an inert seal.

At the sampling location the pump, inlet and outlet pipes, flow meter, acidification assembly, and sample reservoirs were added to the filter compound to form the complete test system. Before the beginning of a run each filter was washed with spring water for approximately 5 minutes in order to remove any carbon fines, and the washings were discharged to the spring via the sampling outlets between the filters. The water flow rate was set at 0.79 gpm (3 liters/min) by adjusting the valve preceding Filter No. 1 and that following Filter No. 4; this provided a 1.9 minute detention time at each filter. The acid pump was activated and adjusted to inject approximately 38 ml/min of 0.4N sulfuric acid solution into the influent to Filter No. 3 (Figure 4, p.24). As described in Appendix A, this flow was found to reduce the pH of the water to the desired 2.5 level. In order to prevent injury to fish and other aquatic life in the pond formed by the spring, the final effluent was returned to the by-pass stream so that it could be neutralized by the by-passed water before it was discharged. The

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*+30 mesh Nuchar, a product of West Virginia Pulp & Paper Co., New York, New York.

by-pass flow was 36 times greater than the filter effluent. The valves at the five sampling outlets (Figure 1a) were adjusted to discharge one drop of water per second into the 20 gallon storage reservoirs. At this rate, an 18 ± 1 gallon composite sample could be collected over a five day period.

The water flow rate and inlet pressure to the system were observed continuously for the first 6 hours of operation; thereafter they were checked daily and adjusted whenever necessary. The total volume of water filtered and the pH of the raw water and effluent from each filter were recorded each day. The 30 gallon acid solution storage tank was filled every other day with 0.4N sulfuric acid. The general condition of the spring and the weather were observed and recorded during each day's check.

At 5 day intervals, the contents of the sample reservoirs were thoroughly mixed and 20 liter volumes were transferred to 5 gallon Pyrex bottles. Two samples were obtained from the raw water reservoir and one from each of the filtered water reservoirs. The water remaining in the reservoirs was discarded and the reservoirs were rinsed and returned to the system. The six bottles were transported to the laboratory where they were stored in a walk-in incubator* at 10°C until they could be solvent extracted.

After approximately 20,000 and 25,000 gallons of water had passed through the filters in the first and second run, respectively, the pumps were shut off and the filters were allowed to drain. The complete filter assembly was transported to the laboratory where the

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*Model 704A Constant Temperature Room, Lab-Line Instruments, Inc., Melrose Park, Illinois.

carbon was removed. The equipment remaining at the sampling location was disassembled and taken to the laboratory for inspection, cleaning, and storage.

2. Laboratory Recovery Procedures.

a. Solvent Extraction.

Trace organic pollutants were recovered from the raw water and filter effluent samples at the natural and adjusted pH levels using chloroform and benzene and a solvent to sample ratio of 1 to 10. The general extraction scheme is outlined in Figure 5. Required pH adjustments in the laboratory were made with 1.0N solutions of hydrochloric acid and sodium hydroxide. Two 10 liter samples were sequentially withdrawn from the 5 gallon bottles stored in the walk-in incubator, starting with the raw water sample, and were placed in two 3.5 gallon Pyrex bottles. The turbidity of the water was noted and the pH was measured and recorded; if necessary, the pH was adjusted to the desired level. The solvent (1 liter) was then added to the sample (10 liters) in three equal portions (333 ml each), and following each addition, the mixture was shaken for a 3 minute interval. The solvent and water phases were allowed to separate; chloroform (1.489 specific gravity) settled to the bottom, while benzene (0.879 specific gravity) floated to the top. The solvent phase containing the concentrated trace organics was siphoned into a 500 ml separatory funnel and after further separation was placed in a 3 liter boiling flask; the water phase was returned to the remaining sample. Another portion (333 ml) of the solvent was added to the 10 liter sample and the procedure was repeated until all the

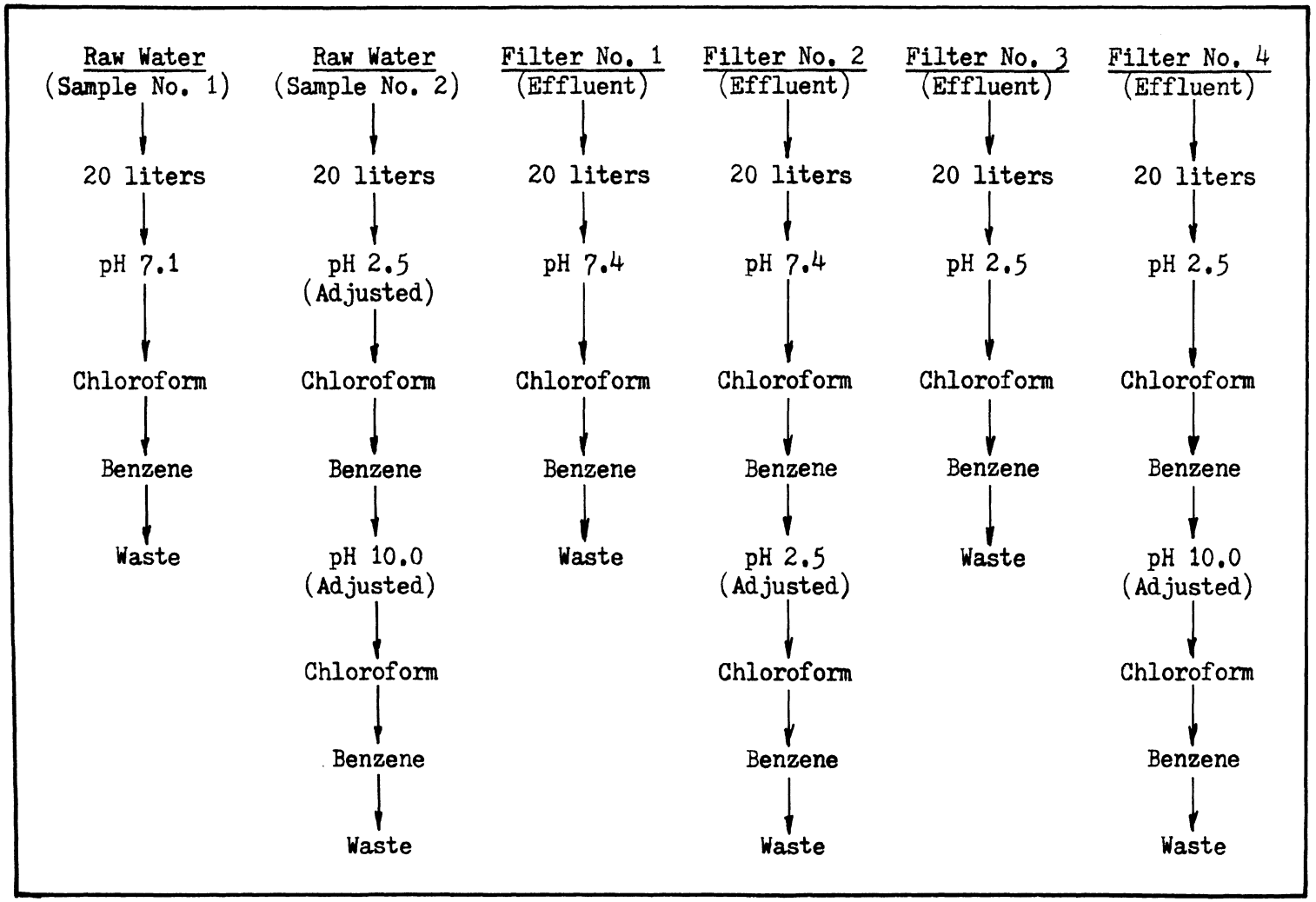

Figure 5

Solvent Extraction Scheme

solvent had been used. Chloroform was first employed and was followed by benzene. The equipment used in the solvent extraction studies is shown in Figure 6.

After all the chloroform or benzene portions had been placed in the 3 liter boiling flask, the solvents were distilled off until a residual volume of approximately 210 ml remained. The residual solvent and concentrated organics were then filtered through a fine sintered glass funnel, and the remaining solvent was evaporated off on a steam bath (Precision No. 66738*) to a volume of approximately 25 ml. The solvent containing the recovered organics was transferred to a numbered (for identification) and tared 16 ml vial which was returned to the steam bath until all solvent had been driven off and constant weight had been obtained. The vial containing the organic extracts was finally stored in the desiccator.

b. Carbon Elution.

At the end of a run, the carbon filters were disengaged from the field test system and brought to the laboratory where the units were opened and the activated carbon was removed and dried. The carbon which was used in the first run was freeze dried.** The material from each filter was distributed in four tared 3 liter boiling flasks, which were then immersed in liquid nitrogen for approximately 30 minutes until the wet carbon was frozen. The flasks and contents were weighed and placed on the freeze drying unit; they were periodically removed from the unit and reweighed

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*A product of Precision Scientific Co., Chicago, Illinois.

**A VirTis Freeze-Mobile, Model 10-145-MR-BA, was used; it was a product of the VirTis Company, Inc., Gardiner, New York. This equipment was available in the Graduate Center for Materials Research, University of Missouri-Rolla.

Figure 6

Equipment Used in Solvent Extraction Studies

until a constant weight had been reached indicating that the carbon was dried. This procedure required 6 days for drying the contents of each filter (24 days for all four filters) and was, therefore, abandoned in the second run in favor of the standard (6, p.216) air drying method. The carbon from each filter was transferred to a wooden tray (24 x 26 x 3 inches) lined with a 4 mil polyethylene sheet and spread out forming a layer which was approximately one inch thick; the trays were then placed in a walk-in incubator* where the carbon was allowed to air dry at 40°C for 5 days while being stirred twice daily. The dried carbon was stored in polyethylene sacks until it could be eluted.

Before the carbon was placed into the Soxhlet extractors for elution with chloroform, the coarse and fine carbon was separated with a No. 12 (1.68 mm opening) sieve. Both coarse and fine carbon was then placed into the Soxhlet extractors with the coarse material forming the bottom one-half layer. In earlier trials with the extractor units, the author had found that the head loss through the fine carbon during the siphoning operation was too high to allow complete draining of the solvent and break of the siphoning cycle. With the coarse layer at the bottom, the head loss was decreased sufficiently to insure proper operation.

Three modified Soxhlet extractors (Pyrex No. 3885**) were used for the elution of the carbon. One of these units, assembled and operating, is shown in Figure 7. The procedure outlined in Standard

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*Model 704 Constant Temperature Room, Lab-Line Instruments, Inc., Melrose Park, Illinois.

**A product of Corning Glass Works, Corning, New York.

Figure 7

Modified Soxhlet Extraction Apparatus

Methods (6, p.217) was followed, except that extraction was continued for only 24 hours (48 cycles) rather than the specified 35 hours. Middleton, et al. (10) have shown that 97 percent of all the material eluted in 46 hours will be recovered in 24 hours (see Literature Review, p.10). After the extraction with chloroform had been completed, the carbon was transferred from the extractor into a porcelain-coated tray and placed under a fume hood until no traces of chloroform remained (approximately 34 hours). The chloroform-extracted carbon was then eluted with benzene for a 24 hour period (48 cycles). Redistilled analytical reagent grade chloroform and benzene were employed.

At the end of an extraction period (24 hours), the eluted organic materials were contained in approximately 2 liters of solvent. The organics were concentrated by distilling off all but approximately 210 ml of solvent. The residual solvent and concentrated organic materials were then filtered through a fine sintered glass funnel to remove particles of carbon which had escaped from the carbon column during the siphoning cycles. The filtered solvent and organics were evaporated on a steam bath until a volume of approximately 75 ml remained. The residual volume was step-wise transferred to a tared 16 ml vial during the first sampling run and a 75 ml bottle during the second sampling run; the larger bottles were used in the second run because they provided a greater surface area and a higher rate of solvent removal. The remaining solvent was evaporated off on the steam bath with final drying in a desiccator. The extracts were dried and periodically weighed until they reached a constant weight. The physical characteristics of the recovered organics were observed and recorded.

Two carbon blanks (wet and dry) were also extracted as described above. The wet blank was prepared by packing a carbon filter with coarse and fine carbon in the predescribed manner; tap water was passed through the filter until the fines had been removed (approximately 5 minutes), the carbon (and water) was retained in the filter for 8 hours, and was then removed, air dried, and eluted with the two solvents. The dry carbon blank consisted of the same amounts of virgin coarse and fine carbon as was used in packing the filters, and was eluted without any prior treatment.

3. Summary of Experimental Conditions.

The experimental conditions employed in the field sampling and laboratory recovery studies are summarized in Table III.

C. RESULTS

1. Meramec Spring Run No. 1.

The first run was started July 10 and continued through August 3, 1969. A total volume of 19,840 gallons of Meramec Spring water was passed through the filters during that period at a rate of approximately 0.79 gpm (3 liters/min). Composite samples for solvent extraction were withdrawn from the 20 gallon reservoirs on July 15, 23 and 29, and on August 3, each time after approximately 4,000 to 6,000 gallons of water had been filtered. At the end of the sampling period, the carbon was removed from the filters and the adsorbed organics were recovered.

The test equipment performed satisfactorily throughout the run with only one minor difficulty which occurred during the first day of operation. Approximately one hour after the test had been started and 50 gallons of water had been filtered, Filter No. 3 failed because

Table III

Evaluation of the Carbon Adsorption Method

a. Summary of Field Sampling Conditions

Run			Av. Spring Flow cfs	Carbon Extraction Data							Solvent Extraction Data			
				Filter Units		Sampling Data					Collected Samples			Water
No.	Length days	Period		No.	Volume* cu. ft.	Flow gpm	Detent. Time min.	pH Filters 1&2	pH Filters 3&4	Volume of Water gal.	Type	No.	Frequency days	Through Filters gal.
1	20	7/10-8/3/69	105	4	0.196	0.79	1.9	7.1	2.5	19,840	Raw water & filter effluents	4	5	5,000**
2	25	11/3-29/69	81							25,680		5		

b. Summary of Laboratory Recovery Conditions

Method	Solvent			pH	Sample Volume	Sample Type
	Type	Solvent/Sample Ratio	Contact Time			
SEM	Chloroform followed by benzene	1/10	9 min.#	2.5 7.1 10.0	20 l. composite samples for each 5,000** gal. of water filtered	Two raw water & four effluents (one for each carbon filter)
CAM		N/A	24 hr.##	7.1 2.5	19,840 gal.-Run No. 1 25,680 gal.-Run No. 2	0.196 cu. ft. activated carbon from each of the four filters

*Each filter; 50% fine, +30 mesh Nuchar C-190, 50% coarse, 4 x 10 mesh Cliffchar; two 3 in. layers of coarse carbon, one on top and one on bottom of a 6 in. layer of fine carbon.

**Approximate average volume.

#Three 3 min. extractions, each with 1/3 of the solvent.

##Serial elution of dried carbon in a modified Soxhlet extractor.

of insufficient packing of the carbon in this unit. This resulted in the displacement of the top stainless steel screen and the flushing away of the carbon into the pipe assembly between Filters No. 3 and No. 4, thus preventing any additional flow through the system. This was not discovered until the following morning (some 16 hours later) at which time these filters were carefully repacked to insure that the screens remained against the support plates and the run was continued.

The pH control in the third and fourth filters was easily maintained throughout the run using an acid pump setting of 55 percent (38 ml/min) and a 0.4N sulfuric acid solution. Approximately six 9 pound bottles of reagent grade acid was used during the sampling run to furnish the necessary total volume of 0.4N solution, and the solution tank required filling every other day. The average pH of the spring water during the run was 7.1, the average effluent pH of the first two filter units was 7.4, and the average effluent pH of the last two filters was 2.5.

The time between sample withdrawals was sufficient to extract the six composite samples following the procedure outlined in Figure 5 (p.31). However, additional time was required to completely evaporate off the solvent on the steam bath. Unfortunately, during the second extraction period the steam bath broke down and replacement parts could not be obtained until two months later. The remaining solvent extracts were, therefore, stored in (9 pound acid) glass bottles, and the procedure was continued after the steam bath had been repaired.

The solvent extraction data are presented in Table IV and the carbon extraction data are given in Table V. The quantities of organics recovered from the four activated carbon filters have been corrected by the amounts of materials extracted from activated carbon blanks (for procedure see p.37) which were as follows:

Type of Blank	Trace Organics Recovered		
	Type	Quantity, grams*	Concentration, µg/gram carbon
Wet	CCE	0.0200	20.0
	CBE	0.0080	8.0
Dry**	CCE	0.0114	11.4
	CBE	0.0062	6.6

*From 520 grams coarse plus 360 grams fine activated carbon.
**Values used in determining actual organic recoveries.

The dry blank values were used because they compared favorably with those obtained by Smith (15) who used the same batch of coarse and fine activated carbon.

The results obtained in Run No. 1 (Tables IV and V) were found to be erratic and considered to be unreliable. The considerable variation in trace organic recoveries was thought to result partly from the unsatisfactory protective finish initially applied to the interior of the carbon filters, the acid solution tank, and the sampling point reservoirs, and partly from the deterioration of the solvent (primarily chloroform) while the extract-solvent mixtures were stored for an extended length of time because of the steam bath failure. When the filters were opened at the end of the run, they still gave off the characteristic solvent odor which was prominent during the curing period that followed the epoxy application. However, the only surface change observed on the various units was

Table IV

Evaluation of the Carbon Adsorption Method

Solvent Extration Data--Meramec Spring Run No. 1

Sampling Data			Raw Water						Effluent*											
Period	Volume of Water Through Carbon gallons								Filter No. 1		Filter No. 2				Filter No. 3		Filter No. 4			
			Sample Volume Extracted, liters																	
			20		20				20		20				20		20			
			pH																	
			7.1		2.5		10.0		7.4		7.4		2.5		2.5		2.5		10.0	
			Type of Trace Organics Recovered																	
Jul.10-Aug. 3	Total	During Period	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE
			Quantity of Trace Organics, grams																	
10-15	3,741	3,741	2.124	1.557	1.274	6.726	15.080	12.673	15.576	15.222	14.864	15.930	1.486	0.637	16.284	15.788	16.355	14.726	14.443	17.629
15-23	9,800	6,059	18.919	22.933	27.748	22.360	26.832	22.360	5.618	23.850	4.357	21.786	5.160	28.322	2.408	26.089	4.472	30.845	3.210	14.791
23-29	15,130	5,330	2.723	4.136	**	3.429	2.017	4.943	**	1.210	**	28.647	0.605	0.504	4.942	0.302	1.109	0.807	0.504	0.908
29-3	19,840	4,910	2.973	1.984	2.323	1.765	1.951	6.690	**	2.973	**	2.044	2.136	1.487	**	2.137	2.788	2.509	1.580	2.044
Total Recovery			26.739	30.610	**	34.280	45.880	46.666	**	43.255	**	68.407	9.387	30.950	**	44.316	24.724	48.887	19.737	35.372
			Concentration of Trace Organics, µg/l																	
8-15	3,741	3,741	150	110	90	475	1,065	895	1,100	1,075	1,050	1,125	105	45	1,150	1,115	1,155	1,040	1,020	1,245
15-13	9,800	6,059	825	1,000	1,210	975	1,170	975	245	1,040	190	950	225	1,235	150	1,135	195	1,345	140	645
23-29	15,130	5,330	135	205	**	170	100	245	**	60	**	1,420	30	25	245	15	55	40	25	45
29-3	19,840	4,910	160	100	125	95	105	360	**	160	**	110	115	80	**	115	150	135	85	110
Average Concentration			368	409	**	458	611	623	**	577	**	912	125	414	**	591	329	651	286	472

*Effluents from Filters No. 1 and 2 had a pH of 7.4, effluents from Filters No. 3 and 4 had a pH of 2.5.

**No values reported; extremely high recoveries were measured and were attributed to chloroform deterioration during the prolonged storage of the chloroform-organics solution.

Table V

Evaluation of the Carbon Adsorption Method
Carbon Extraction Data--Meramec Spring Run No. 1

Sampling Data			Filter No.	Trace Organics Recovered					
							Physical Characteristics		
Period	Volume of Water Through Carbon gallons	pH		Type	Quantity grams	Concentration µg/l	Color	Form	Odor
July 10 to August 3, 1969	19,840	7.1-7.4	1	CCE CBE CCE+CBE	0.7150 0.0083 0.7233	9.53 0.11 9.64	Dark Brown Light Brown	Solid Solid	Chemical-musty Medicinal
			2	CCE CBE CCE+CBE	0.1986 0.0146 0.2132	2.65 0.19 2.84	Dark Brown Light Brown	Solid Solid	Chemical-musty Medicinal
		2.5	3	CCE CBE CCE+CBE	0.4379 0.0236 0.4615	5.84 0.32 6.16	Dark Brown Yellow	Highly Viscous Highly Viscous	Chemical-sweet Medicinal
			4	CCE CBE CCE+CBE	0.2948 0.0125 0.3073	3.93 0.17 4.10	Dark Brown Yellow	Highly Viscous Highly Viscous	Chemical-sweet Medicinal

that of the acid solution storage tank. The acid had changed the surface texture and the finish had developed blisters over the area in contact with the acid solution. It should be pointed out that the solvents used in this Phelan Faust epoxy finish were of the high boiling point type and the curing procedure prescribed by the manufacturer did not result in the complete evaporation of the solvents.

Although the recovery data were not satisfactory, this run served as a guide in evaluating the field sampling procedures developed for this study and provided the investigator with practical experience in effectively performing the necessary operational tasks. The most valuable findings during this first run were the significant recoveries of trace organics obtained with the SEM from the spring water and filter effluents, and the successful operation of the test equipment.

2. Meramec Spring Run No. 2.

Because of the possible epoxy solvent contamination and chloroform deterioration during the first run at Meramec Spring, it was felt necessary that a second run be performed which would be essentially identical to the first. Run No. 2 was started after the initial protective coating had been removed and a new epoxy finish had been applied and cured (see p.21). The new coating was very satisfactory and there was no trace of solvent odor after the curing procedure or after the sampling run; in addition, the protective surface was not visually altered in any way during the run.

The second run was started on November 3 and continued through November 29, 1969. A total volume of 25,680 gallons of spring water

was passed through the filters during that period at a rate of approximately 0.79 gpm (3 liters/min). Composite samples for solvent extraction were withdrawn on November 7, 13, 18, 24 and 29, each time after approximately 4,000 to 6,000 gallons of water had been filtered. At the end of the sampling period, the carbon was removed from the filters and the adsorbed organics were recovered.

The atmospheric temperature during this sampling period ranged from 73°F (November 4) to 15°F (November 14) and the electric heater operated about 30 percent of the time. This heater maintained the temperature on the equipment-support platform so that the filter units and especially the solvent extraction sampling outlets and reservoirs would not freeze.

Difficulty was encountered because of temporary clogging of Filters No. 3 and 4. On November 18, during the second week of operation, Filter No. 4 became slightly plugged; it was, therefore, necessary to increase the pumping pressure through the filter units from the normal operational level of 7 to 10 psi. The effluent ran slightly cloudy for a brief period (3 minutes) after the pressure had been increased; this cloudy (milky-gray) appearance may have been due to a sloughing off of material that had built up on the carbon because of the low pH maintained in this unit during the run. After three days of operation at the increased pressure, the filter began to operate normally and the pressure was reduced to the original level. This same problem developed again on November 26, however, this time it was Filter No. 3 which exhibited signs of being plugged. The pressure was increased to 10 psi once more and remained there throughout the last three days of the run without any further difficulty.

During the week preceding the first increase in pumping pressure (November 8 to 12), the spring showed a slight turbidity (milky-cloudy appearance) as did the well waters in the St. James, Missouri, area.* It had rained before and during these five days and the turbidity increase of the spring water was a natural phenomenon; nonetheless, the high turbidity present in the St. James well waters was more unusual, and this dictated the need for recording this event. The higher spring turbidity could have been the reason for the effluents of the last two filters becoming murky, however, the effluents of the first two filters showed no change at any time during the run and the activated carbon retained its natural black color when removed from all of the filters at the end of the run.

The solvent and carbon extraction data are presented in Tables VI and VII, respectively, and are graphically shown in Figure 8. The quantities of trace organics recovered from the four activated carbon filters have been again corrected by the amounts of materials extracted from a dry carbon blank (see p.40). The physical characteristics of the CCE and CBE are also shown in Table VII. The characteristics of the SCE and SBE of the filter effluents appeared to be similar to the corresponding CCE and CBE, however, their amounts were so infinitesimal that it was not practical to record their physical characteristics with any degree of surety.

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*This was reported by residents of St. James who were employed by the James Foundation at the Meramec Spring Park.

Table VI

Evaluation of the Carbon Adsorption Method
Solvent Extraction Data--Meramec Spring Run No. 2

Sampling Data			Raw Water						Effluent*											
Period	Volume of Water Through Carbon gallons								Filter No. 1		Filter No. 2				Filter No. 3		Filter No. 4			
			Sample Volume Extracted, liters																	
			20		20				20		20				20		20			
			pH																	
			7.1		2.5		10.0		7.4		7.4		2.5		2.5		2.5		10.0	
			Type of Trace Organics Recovered																	
Nov.	Total	During Period	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE	SCE	SBE
			Quantity of Trace Organics, grams																	
3-7	4,190	4,190	2.695	1.665	1.823	1.586	1.189	1.905	2.380	1.348	2.300	1.428	1.586	1.905	2.620	1.586	2.065	1.508	0.874	1.348
7-13	9,360	5,170	2.930	1.955	2.440	1.465	1.875	2.735	4.300	1.955	2.050	1.857	2.050	2.050	2.735	2.245	3.615	1.955	1.857	1.857
13-18	14,180	4,820	2.050	1.732	1.552	1.460	8.940	2.190	2.282	3.470	1.552	1.642	1.005	1.918	1.733	1.642	1.642	0.730	0.547	0.822
18-24	20,165	5,985	0.566	0.794	1.132	1.815	0.907	2.265	1.472	1.928	1.021	2.380	1.021	1.475	0.453	3.630	1.815	1.701	1.247	0.113
24-29	25,680	5,515	3.330	1.980	2.290	6.560	1.355	1.562	1.250	1.562	3.125	1.978	2.915	1.875	7.700	2.085	1.980	4.580	1.562	6.250
Total Recovery			11.571	8.126	9.237	12.886	14.248	10.657	11.684	10.263	10.048	9.285	8.577	9.223	15.241	11.188	11.117	10.474	6.087	10.787
			Concentration of Trace Organics, µg/l																	
3-7	4,190	4,190	170	150	115	100	75	120	150	85	145	90	100	120	165	100	130	95	55	85
7-13	9,360	5,170	150	100	125	75	95	140	220	100	105	95	105	105	140	115	185	100	95	95
13-18	14,180	4,820	110	95	85	80	490	120	125	190	85	90	55	105	95	90	90	40	30	45
18-24	20,165	5,985	25	35	50	80	40	100	65	85	45	105	45	65	20	160	80	75	55	5
24-29	25,680	5,515	160	95	110	315	65	75	60	75	60	95	140	90	370	100	95	220	75	300
Average Concentration			119	84	96	133	146	109	120	105	103	95	88	95	157	115	114	107	63	111

*Effluents from Filters No. 1 and 2 had a pH of 7.4, effluents from Filters No. 3 and 4 had a pH of 2.5.

Table VII

Evaluation of the Carbon Adsorption Method
Carbon Extraction Data--Meramec Spring Run No. 2

Sampling Data			Filter No.	Trace Organics Recovered					
							Physical Characteristics		
Period	Volume of Water Through Carbon gallons	pH		Type	Quantity grams	Concentration µg/l	Color	Form	Odor
November 3-29, 1969	25,680	7.1-7.4	1	CCE CBE CCE+CBE	0.7311 0.0200 0.7511	7.52 0.21 8.73	Dark Brown Light Brown	Solid Solid	Chemical-musty Medicinal
			2	CCE CBE CCE+CBE	0.2314 0.0098 0.2412	2.48 0.10 2.58	Dark Brown Light Brown	Solid Solid	Chemical-musty Medicinal
		2.5	3	CCE CBE CCE+CBE	0.4436 0.0099 0.4535	4.56 0.10 4.66	Dark Brown Yellow	Highly Viscous Highly Viscous	Chemical-sweet Medicinal
			4	CCE CBE CCE+CBE	0.3699 0.0176 0.3875	3.81 0.18 3.99	Dark Brown Yellow	Highly Viscous Highly Viscous	Chemical-sweet Medicinal

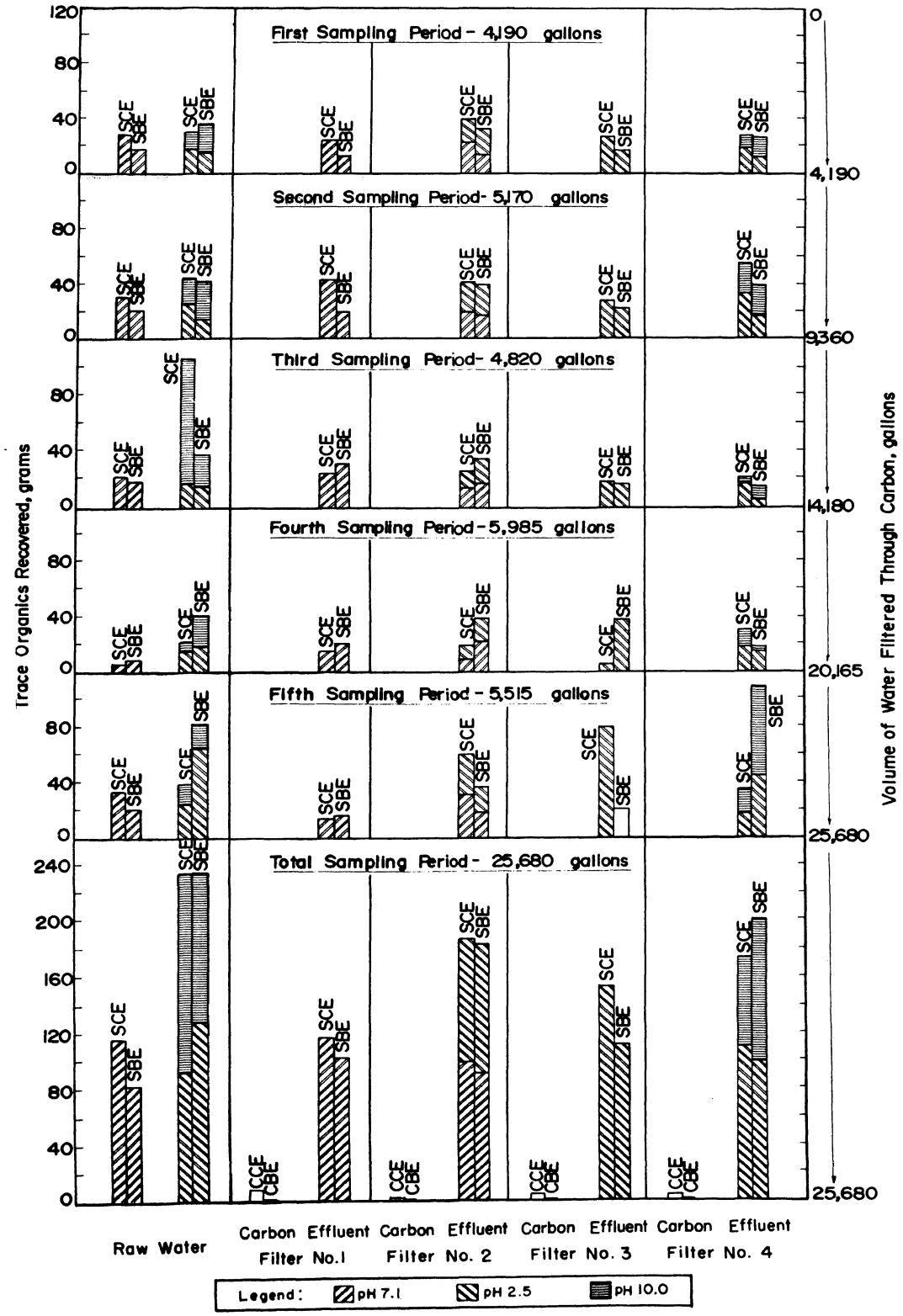

Figure 8

Evaluation of the Carbon Adsorption Method
Solvent and Carbon Extraction Data--Meramec Spring Run No. 2

The data from both the solvent extraction and carbon elution studies showed that the spring contained trace organic pollutants, but the two values did not compare as expected. The raw water (natural pH) SCE and SBE average concentrations for the entire run were 119 and 84 µg/l, respectively, whereas the CCE and CBE from the first carbon filter were only 7.5 and 0.2 µg/l, respectively. A similar relationship existed between the total quantity of organics recovered from a filter effluent and the amount of material desorbed from the carbon of the following filter in the series. Sequential extraction of the raw spring water at pH 2.5 and 10.0 resulted in a two-fold increase in the recovery of SCE and SBE materials, as compared to the amounts obtained with a single extraction at the natural pH of 7.1.

The CCE recovered from the dry activated carbon blank was approximately 1.6, 4.9, 2.6, and 3.1 percent of the CCE recovered* during the run with Filters No. 1, 2, 3, and 4, respectively. The CBE eluted from the dry blank represented a greater percentage of the total recovery from each unit than did the CCE; the blank CBE was approximately 31, 63, 62, and 35 percent of the CBE recovered* with Filters No. 1, 2, 3, and 4, respectively.

At the end of the run it was realized that the equipment had performed satisfactorily as a compact, easy to assemble and maintain unit. If there are no major preliminary site preparation requirements, the equipment can be assembled by one person and be operating in less than eight hours.

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*These values refer to actual recoveries before blank correction.

V. DISCUSSION

The equipment and procedures developed during this investigation formed a test system which could be effectively employed in the evaluation of the carbon adsorption method (CAM) under field conditions and depended upon the solvent extraction method (SEM) to monitor the concentration of trace organic substances in the filter influent and effluent. Preliminary studies using this system have indicated that the CAM had a low total (adsorption-desorption) efficiency for recovering trace organics from natural water, however, more work is needed in order to fully evaluate the method and establish its limitations.

The (0.196 cubic foot) activated carbon filter units, which were an integral part of the field test system, incorporated the basic concepts of both the large (1.5 cubic foot) and small (0.073 cubic foot) filters used in previous investigations. The large number (five) of filters available was capable of meeting many different experimental conditions, including the need for pretreatment, operation in series or in parallel, and pH adjustment; and the location of the sampling outlets was selected to enable the monitoring of the influent to and effluent from each filter. The total system formed a rugged, compact, self-contained, mobile arrangement which would effectively serve a wide variety of field applications.

During the preliminary field investigation, various operational parameters were investigated in order to establish guidelines for the effective application of the test system. The size of the sample to be filtered (20,000 to 25,000 gallons) was selected to be well in excess of the recommended sample volume for the standard filter (5,000 gallons) properly adjusted for the larger size of the test

filters. Since the filters used in this investigation were approximately three times as large as the standard filter, 15,000 gallons would have been the recommended size; however, this volume was increased to 20,000 or 25,000 gallons in order to investigate the possible breakthrough of organic matter through the carbon columns. The total volume was divided into smaller increments (4,000 to 6,000 gallons) for the parallel solvent extraction studies in an attempt to determine the time at which each filter became overloaded and to evaluate the relative efficiency of the filters during the run. Because earlier studies (1, 28) at Meramec Spring had indicated a relatively low concentration of trace organics in the spring water, the volume of sample (20 liters) selected for the solvent extraction studies had to be sufficient to insure measurable recoveries. However, the sample size was also dictated by the need to extract and process a large number of samples during the five day period between sample collections. A total of 18 different extractions were performed on the six samples taken during each sampling period in order to allow use of two different solvents (chloroform and benzene) and extraction at three different pH levels (natural, 2.5, and 10.0). The flow rate through the filters was daily set at 0.79 gpm (3 liters/min) giving a contact time of 1.9 minutes. However, on the basis of the total volume of water filtered, the flow rate during the first run averaged only 0.61 gpm and during the second run 0.71 gpm. The corresponding detention times were 2.4 and 2.1 minutes, respectively, and compared favorably with the values employed by other investigators. The system was designed so that the flow rate could be varied over a wide range, and consequently the contact time could

be adjusted to different levels to permit the evaluation of the effect of this variable.

The average concentrations of trace organics recovered from Meramec Spring water by solvent extraction and carbon adsorption in Run No. 2 are summarized in Table VIII. The concentration of SCE and SBE in the spring water (119 and 84 µg/l, respectively) compared favorably with the quantity of SCE and SBE recovered by Chang (28) from the same water (96.3 and 194.4 µg/l, respectively) in the winter of 1969. Chang also extracted Meramec Spring water sequentially at pH 4 and 10 and found that pH adjustment resulted in increased SCE and SBE recoveries. However, he extracted the water at the two pH values with either chloroform or benzene; consequently his data cannot be directly compared to the findings of this study where chloroform extraction was always followed by benzene extraction (see Figure 5, p.31). The concentration of CCE and CBE in the spring water was, on the other hand, much lower than the values reported by Grigoropoulos and Smith (1). These investigators used three large carbon filters in series and sampled Meramec Spring water at its natural pH in two runs made during the winter of 1966; they eluted the carbon with both chloroform and benzene, however, they followed chloroform extraction with ethanol and in some cases acetone extraction before using benzene. Because of the different experimental conditions employed, it is possible to compare only the CCE recovered by their first two filters to the values determined in the present study. On this basis, the CCE concentrations obtained by Grigoropoulos and Smith in their two runs (30.4 and 51.7 µg/l with the first filter and 10.8 and 21.8 µg/l with the second filter) were four to seven or eight times

Table VIII

Evaluation of the Carbon Adsorption Method
Average Recoveries--Meramec Spring Run No. 2

Filter No.	pH of Water	Chloroform Extract					Benzene Extract				
		Organics, µg/l		% Recovery	Recovery % of Filter No.		Organics, µg/l		% Recovery	Recovery % of Filter No.	
		in Filter Influent	Eluted from Carbon		1	3	in Filter Influent	Eluted from Carbon		1	3
1	7.1	119	7.5	6.3	100	N/A	84	0.2	0.24	100	N/A
2	7.4	120	2.5	2.1	33.3	N/A	105	0.1	0.09	37.5	N/A
3	2.5	88	4.6	5.2	61.4	100	95	0.1	0.11	45.8	100
4*	2.5	157	3.8	2.4	50.6	82.6	115	0.2	0.17	70.8	200

*The effluent from this filter contained 114 µg/l SCE and 107 µg/l SBE (when solvent extracted at pH 2.5).

greater than the values obtained in this study (7.5 and 2.5 µg/l with the two filters). The second filter employed by Grigoropoulos and Smith recovered approximately 35 to 42 percent of the amount of CCE recovered with the first unit and this is also true in the present study where the corresponding value was 33 percent. Lowering of the pH of the water before it entered Filter No. 3 significantly increased the amount of CCE and CBE recovered by this filter as well as Filter No. 4 (Table VIII).

Comparison of the solvent extraction and carbon adsorption data (Table VIII) would indicate that the CAM had an apparent recovery efficiency which was considerably lower than the values determined by Hoak and others (7) in batch laboratory studies using phenol which ranged from 19 to 77 percent. In fact, if the average concentration of SCE and SBE over the total sampling period is considered, it would appear that the effluent from Filters No. 1 and 3 had a greater trace organics content than the corresponding influent to these filters. To further verify this observation, the total concentration of solvent extracts (both chloroform and benzene) obtained from the influent to and effluent from each filter during each sampling period is presented graphically in Figure 9. In preparing this figure, only the SCE and SBE materials recovered by extraction at the pH of the water passed through the corresponding filter have been considered. The arithmetic difference between the influent and effluent concentration for any given filter and at any given time has been indicated in Figure 9 as either adsorption (+) or desorption (-). During the first sampling period, Filter No. 1 appeared to be adsorbing organics, whereas during the second, third,

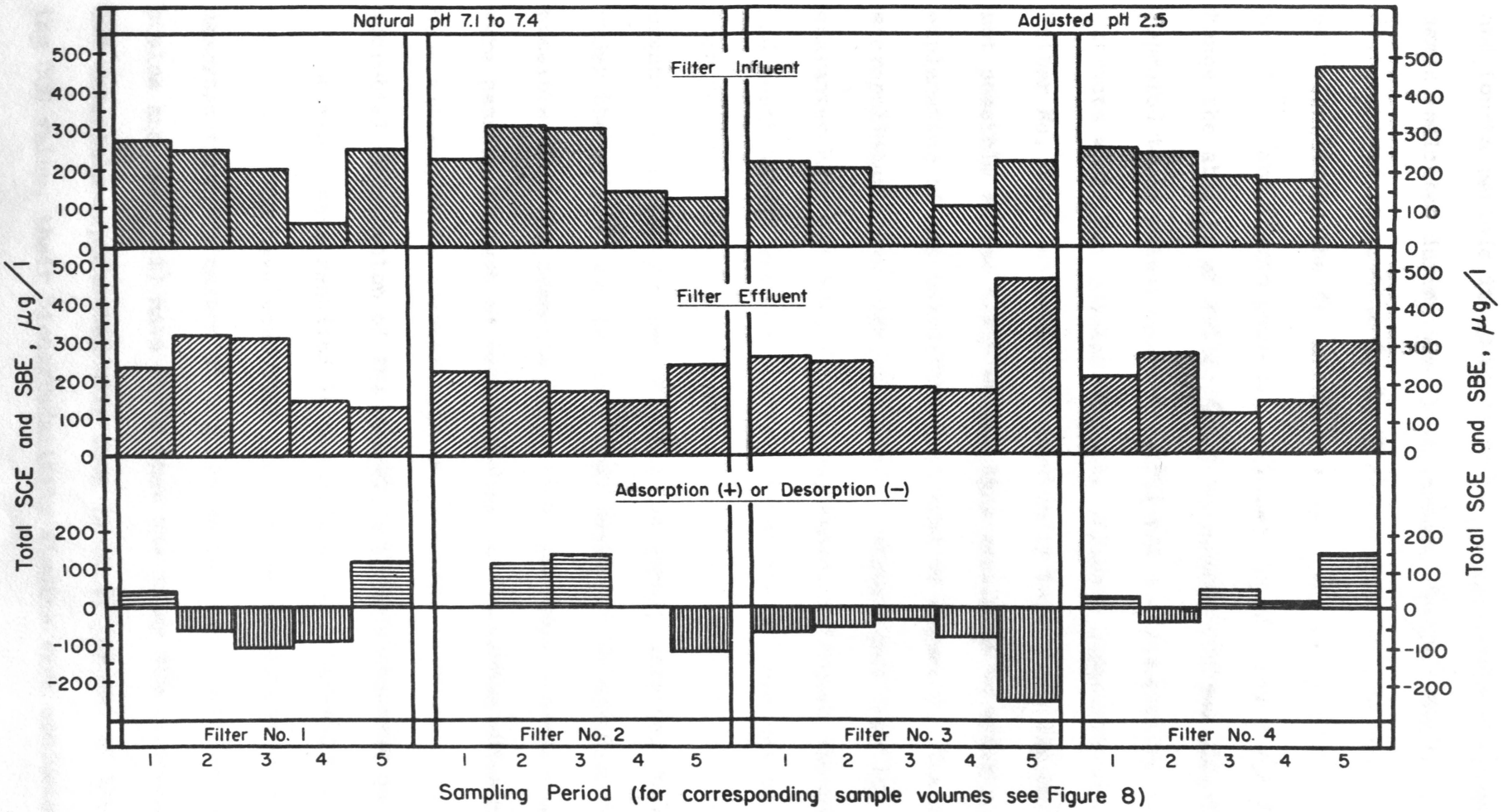

Figure 9

Evaluation of the Carbon Adsorption Method
Meramec Spring Run No. 2

and fourth periods it appeared to be losing organics; adsorption was again indicated during the fifth period. On the contrary, Filter No. 2 showed adsorption during the second and third periods and desorption during the fifth, while showing neither gain nor loss during the first and fourth periods. Although pH adjustment seemed to enhance the ability of Filter No. 3 to recover CCE and CBE, this filter appeared to be releasing in its effluent a concentration of solvent extracts which was greater than the influent concentration. Finally Filter No. 4 gained material essentially throughout the run. It is not possible on the basis of the data available to offer a complete explanation of the conditions indicated by Figure 9. The organic micropollutants are complex materials whose exact identity and character have not been fully established. Although the qualitative and quantitative recovery efficiency of the SEM has not actually been determined, it is reasonable to assume that all the trace organic materials present in the water sample were not recovered under the solvent and pH conditions employed; in addition it is possible that the organics might have undergone changes while they were passing through or were adsorbed on the carbon which could have altered their solvent extraction characteristics. Partial microbial degradation of the organic materials adsorbed on the carbon might have resulted in the release of intermediates, and this could also have accounted for the low concentration of organics desorbed from the carbon at the end of the run. Although Grigoropoulos and Smith (1) have found that the 5 day BOD of Meramec Spring CCE materials represented only from 11 to 19 percent of the corresponding COD value, their biodegradability studies were conducted using

extracts that had been actually recovered from the carbon and do not necessarily reflect what had happened while the organics were sorbed on the carbon. Better knowledge of the character of the trace organic substances recovered by solvent extraction and carbon adsorption would be of great value in the further evaluation of the two recovery techniques, and research is urgently needed in this important aspect of the trace organics problem.

Obviously this study has left many questions unanswered. Yet it represents the first study that has been performed to evaluate the CAM using the actual organic materials which are found in natural water; and has been conducted under actual field conditions. From the operational viewpoint, additional work at various flow rates through the carbon is needed in order to evaluate the effect of contact time on sorption efficiency. The size of the sample which is solvent extracted should be increased to provide a more significant quantity of organics which will not only improve the reliability of determination but will also provide sufficient sample for characterization studies. Batch-type solvent extraction, however, is a tedious and time consuming operation and the size of sample to be extracted would be limited by practical considerations; the development of a continuous flow solvent extractor would effectively overcome this difficulty. The number of raw water and filter effluent samples collected over the sampling period was also dictated by the time required to extract some 18 different samples. More frequent sampling during the early part of the run would have been desirable and could have been accomplished with a continuous flow extractor. Finally, other sources and types of water which might contain different types

of trace organic pollutants and at different concentration levels should be employed in the evaluation of the CAM in order to develop a range of operational parameters, including flow rate and contact time, frequency of sampling, size of sample to be filtered and size of sample to be solvent extracted, pH, and appropriate solvents.

VI. CONCLUSIONS

On the basis of the findings of this study, the following conclusions may be drawn.

1. The test system developed during this investigation proved to be satisfactory for the field evaluation of the carbon adsorption method with parallel solvent extraction studies and enabled the monitoring of the trace organic materials in the influent to and effluent from the carbon filters.
2. The preliminary evaluation of the carbon adsorption method using this test system indicated that the method had a low total efficiency for recovering trace organic pollutants from Meramec Spring water; however, further research is needed in order to fully evaluate the method and establish its limitations.
3. The adjustment of the pH of the spring water and effluents from the carbon filters to 2.5 and 10 significantly increased the concentration of trace organics recovered with solvent extraction, and the lowering of the pH of the spring water to 2.5 significantly increased the concentration of trace organics recovered by carbon adsorption.
4. The spring water SCE and SBE materials averaged 119 and 84 µg/l, respectively, during a 27 day sampling period; an average of 10 µg/l CCE and 0.3 µg/l CBE were recovered by two carbon filters in series during this period and an additional 8.4 µg/l CCE and 0.3 µg/l CBE were obtained with two more filters in series after the pH of the water had been adjusted to 2.5.
5. In order to fully evaluate the carbon adsorption method using the test system and experimental procedures developed in this

study, additional sources and types of water should be employed and the flow rate through the carbon and frequency of solvent extraction should be varied. In addition, the character of the solvent and carbon extracts should be established.

VII. RECOMMENDATIONS FOR FUTURE WORK

On the basis of the findings of this study, the following areas of further research are recommended.

1. The recovery efficiency of the carbon adsorption method should be evaluated during the early part of a run (less than 4,000 to 5,000 gallons of water filtered) in order to assure that the carbon had not been overloaded.
2. A continuous flow solvent extraction system should be developed in order to enable extraction of a large size sample and recovery of a significant quantity of trace organics.
3. The trace organic substances recovered with both solvent extraction and carbon adsorption should be characterized using advanced analytical instrumentation in order to allow the qualitative evaluation and comparison of the two recovery methods.
4. Additional studies using different flow rates through the carbon, sampling sources, pH adjustment schemes, and filter arrangements are necessary for the complete evaluation of the carbon adsorption method using parallel solvent extraction.

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APPENDIX A

Acid Solution Pump Setting

A special pump was used to inject an acid solution into the test system between Filter No. 2 and Filter No. 3. A variable output diaphragm pump* was selected for this purpose, and was used in conjunction with a 30 gallon acid solution tank and mixer (Figure 4, p.24). The maximum output of the pump was 70 ml/min and the manufacturer recommended that it be run at 40 to 70 percent of its maximum capacity.

A titration curve (Figure A-1) was prepared for Meramec Spring water using 0.4N sulfuric acid. Approximately 11.5 ml of 0.4N acid were required per liter of water to reduce its pH to the 2.5 value. Since the flow through the activated carbon filters was to be 3 liters/min, a 35 ml/min acid solution feed would be required.

A pump setting of 50 percent (5 on the pump dial) would give an approximate flow rate of 35 ml/min. This setting was initially used, however, after operating the actual test system for a few hours, it was found that a pump rate of 55 percent (5.5 on the dial) was necessary to provide the desired pH control.

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*Wallace & Tiernan No. 94-110, purchased from Lesco Division of Sidener Supply Co., Granite City, Illinois.

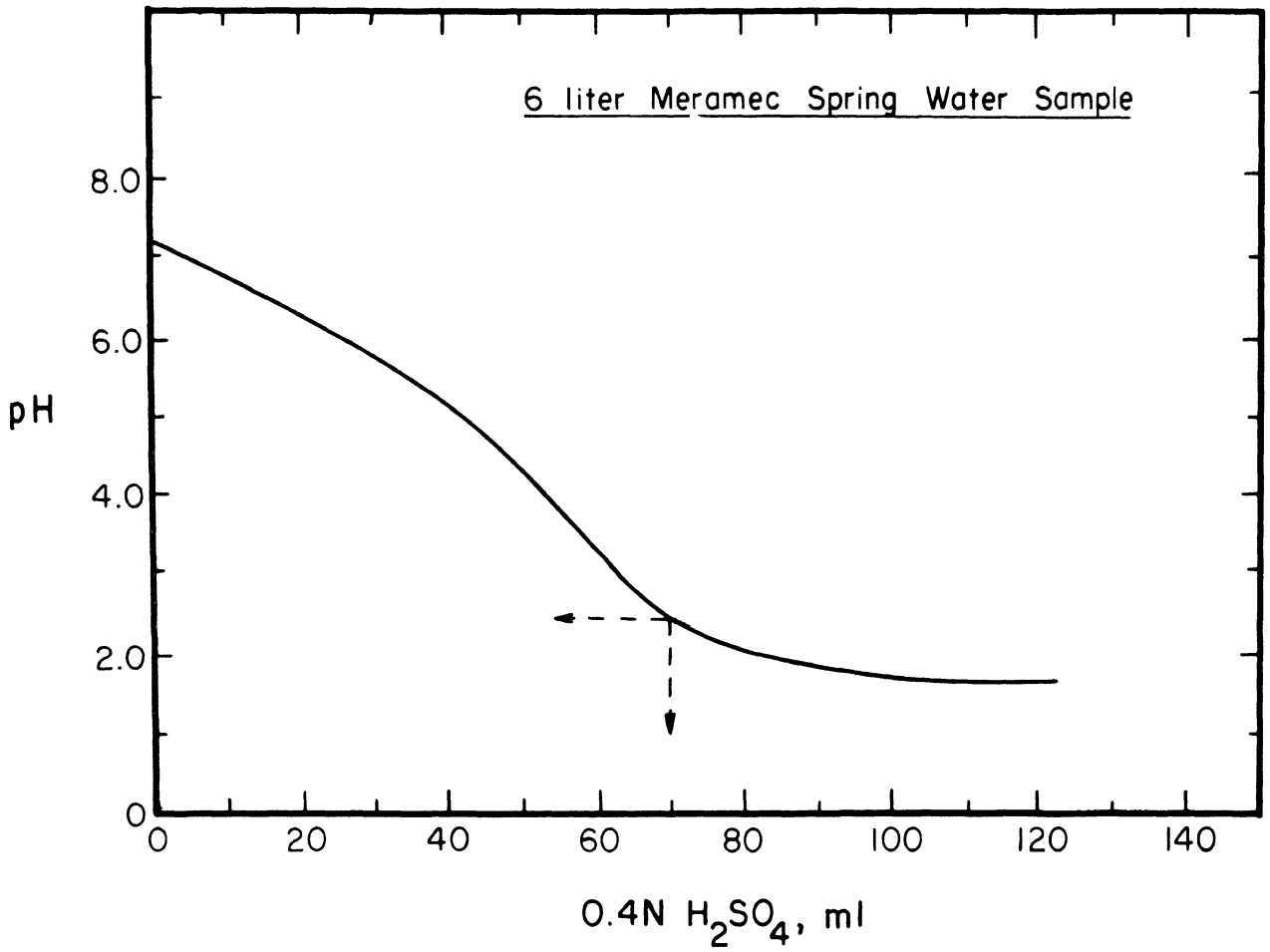

Figure A-1

Titration Curve for Meramec Spring Water

VITA

Stanley Kent Wagher was born on June 10, 1944, in Princeville, Illinois. He received his primary education in Victoria, Illinois, and his secondary education in Oneida, Illinois. He received a Bachelor of Science degree in Civil Engineering from the University of Missouri-Rolla, Rolla, Missouri, in May 1968.

He was enrolled in the Graduate School of the University of Missouri-Rolla working toward a Master of Science degree in Civil (Sanitary) Engineering from June 1968 to January 1970 and during this period he was awarded a Federal Water Quality Administration Traineeship. He is presently serving his two year ROTC Commission obligation in the Medical Service Corps, U.S. Army.

He was married to Judith Annette Jensen of Rolla, Missouri, on June 8, 1968, and they have a son, Nathan Michael.